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Controlled Grain Boundary Structures in Superconductors

by

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ABSTRACT

Theoretical work supported by this grant has led to the concept of the specific pinning force (Q) and the development of new methods to sum elementary interaction forces to find Q . Pinning due to changes in transition temperature or thermodynamic critical field in thin layers (e.g., a grain boundary), is greatly reduced due to the proximity effect and the stress field interaction due to the dislocations in the grain boundary has been shown to be negligible. The crystalline anisotropy (CA) and electron scattering (ES) interactions have been computed for the first time for an arbitrary boundary. The CA interaction decreases, whereas the ES interaction increases, with increasing impurity content; the CA interaction decreases more rapidly with temperature than does the ES interaction. Only for very high purities is the magnitude of the CA interaction predicted to exceed that of the ES interaction. Experiments on niobium bicrystals, polycrystalline niobium thin foils doped with oxygen, lead-bismuth alloy thin films and lead-bismuth alloy films in which either lead or thallium has been allowed to diffuse down the grain boundaries and out into the grains provide evidence that confirms the predictions of the theory. In particular increasing impurity doping levels increase the Q of grain boundaries dramatically, a finding that is only consistent with an ES interaction which dominates grain boundary pinning. These results suggest that further improvements in grain boundary pinning in the A-15 compounds, which are relatively high purity, are possible by decreasing their impurity content if that can be accomplished without decreasing their thermodynamic critical field or transition temperature.

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MATTHEW J. KERPER
Chief, Technical Information Division

Brief Outline of Major Results Under This Grant

Theoretical:

The critical current or current carrying capacity of a superconductor depends on pinning a lattice of flux lines (FLL). Major issues are 1) What the mechanism and magnitude of the elementary interaction force between a single lattice defect and the FLL and 2) How to sum these interaction forces to obtain the total pinning force F_p . Important progress was made on both these issues. On the summation problem a new concept was introduced⁽¹⁾, the specific pinning force Q obtained by dividing F_p by either the defect density for point defects such as small voids or the total defect area for planar defects such as grain boundaries. By plotting Q vs f_p , the elementary interaction force, for defects where the latter can be computed with confidence, empirical summation curves were constructed which can be used to solve the summation problems where f_p cannot be computed accurately⁽²⁾. By comparing the Q 's of thin normal precipitates with those of voids of the same volume using these curves, it was found that the precipitate f_p was up to 3 orders of magnitude smaller than that of a void. The difference was attributed to the proximity effect which induces superconductivity in the normal particle and a theory was developed which gave good agreement with the correction observed to be necessary⁽³⁾. This theory also means that the change in transition temperature T_c or thermodynamic critical field H_c of the thin layer of atoms in a grain boundary cannot produce a significant elementary interaction force. In agreement with this prediction, thin normal metal layers (Al) interspersed between layers of PbBi alloy in multilayer films were found to have negligible pinning effect. If, however the normal layer was antiferromagnetic chromium, large Q 's due to each layer were observed⁽¹⁰⁾. This effect is attributed to the breaking of superconductivity electron pairs by defects in the magnetic ordering on the surface of the chromium. This means that there will be a region approximately a coherence length ξ in width adjacent to each layer in which

the superconducting order parameter is depressed. This region can strongly pin flux lines even if the chromium layer is quite thin.

There are three possible elementary interaction mechanisms for grain boundaries. These include:

1. The interaction between the grain boundary and the FLL due to the interaction between the strain field of the boundary and the stress field of the FLL. This is called the stress field (SF) interaction.

2. The interaction between the grain boundary and the FLL due to the anisotropy of the upper critical field H_{c2} . This is called the crystalline anisotropy (CA) interaction.

3. The interaction between the grain boundary and the FLL due to scattering of electrons from the boundary. This is called the electron scattering (ES) interaction.

To estimate the magnitude of these interactions it was first necessary to develop methods for computing \hat{f}_p , the elementary interaction force per unit area of a single planar defect. Wilson Yetter developed a particularly simple method using Fourier transforms as part of his Ph.D. theses^(6,11).

Using this method it was shown theoretically that the stress field interaction will be negligible for any grain boundary in which dislocations are closely spaced (i.e., a high angle grain boundary) and to be quite small even for low angle boundaries. Experimentally no flux pinning from low angle grain boundaries can be detected in either niobium bicrystals or polygonized single crystals⁽⁵⁾. The evidence thus suggests that the SF interaction is negligible for all boundaries.

The crystal anisotropy interaction has been estimated by us to be

$$(\hat{f}_p)_{CA} = \frac{(1-b)}{3} \mu_0 H_c^2 \left(\frac{\delta H_{c2}}{H_{c2}} \right) \quad 1)$$

where b is the reduced magnetic induction, H_c is the thermodynamic critical field and $\delta H_{c2}/H_{c2}$ is the relative change in upper critical field across the boundary. Since the magnitude of the H_{c2} anisotropy decreases with increasing impurity content (a convenient measure is the impurity parameter $\alpha = 0.88 \xi_0/\ell$ where ξ_0 is the BCS coherence length and ℓ is the electron mean free path) $(\hat{f}_p)_{CA}$ should decrease with impurity additions. The temperature dependence of the CA interaction may be described by that of the ratio

$$\frac{(\hat{f}_p)_{CA}}{\mu_0 H_c^2} = \frac{1-b}{3} \frac{\delta H_{c2}}{H_{c2}} \approx \frac{1-b}{3} \frac{\delta H_{c2}^{(0)}}{H_{c2}} (1-t) \quad 2)$$

where $t = T/T_c$.

The electron scattering interaction also has been computed⁽⁷⁾. The assumptions are as follows: 1) Electrons are scattered with a probability β from the boundary. Experimental and theoretical evidence suggests that strong electron scattering occurs at the dislocation cores which make up the boundary and thus that $\beta \approx 1$ for random high angle grain boundaries. 2) Using the $\beta = 1$ hypothesis, ℓ is computed as a function of distance x from the boundary; ℓ varies from $\ell_B/2$ at the boundary to ℓ_B far from the boundary (ℓ_B = the background electron mean free path). 3) A local relation between the Guizburg-Landau parameter κ and ℓ is assumed which allows the $\Delta\kappa(x)$ profile near the boundary to be computed. At high fields the ES interaction is estimated to be

$$(\hat{f}_p)_{ES} = \frac{\sqrt{2\pi}}{3} (1-b) \mu_0 H_c^2 g_1 \frac{\tilde{\Delta}\kappa}{\kappa} (g_1) \quad 3)$$

where g_1 is the shortest reciprocal lattice vector of the FLL and $\tilde{\Delta}\kappa(g_1)/\kappa$ is the one-dimensional Fourier transform of $\kappa(x)$ evaluated at g_1 . Again it is useful to form the ratio

$$\frac{(\hat{f}_p)_{ES}}{\mu_0 H_c^2} = \frac{\sqrt{2\pi}}{3} (1-b) g_1 \frac{\tilde{\Delta}\kappa(g_1)}{\kappa} \sim (1-t)^{1/2} \quad 4)$$

This ratio decreases more slowly with $(1-t)$ than that for the CA interaction. In addition the dependence on impurity content is opposite than that of CA; the $(\hat{f}_p)_{ES}$ increases strongly as d is increased to a maximum at $\alpha \approx 10$. Thus measurements of grain boundary specific pinning force Q as a function of sample purity and temperature should allow one to say whether CA or ES is dominant.

The theory makes a clear prediction in this regard. The electron scattering interaction is predicted to be larger than the CA interaction for α 's above ~ 0.03 in both niobium and $Nb_3Sn^{(13)}$. One thus expects the ES interaction to dominate in all but the purest materials (below a resistivity ratio of ~ 500 in Nb and below a resistivity ratio of ~ 30 in Nb_3Sn).

Experimental:

An important difficulty in interpreting the results of grain boundary flux pinning experiments is that the measured F_p is usually the sum of the \hat{f}_p of many grain boundaries. While one expects the Q_{GB} measured to be close to the average value of \hat{f}_p one cannot easily study the effects of grain boundary character. Das Gupta, Koch, Kroeger and Chou showed however that by measuring the anisotropy of F_p for a bicrystal one could determine Q_{GB} for a single grain boundary. Unfortunately, they could only grow rather pure symmetric bicrystals from the melt and thus were unable to test either the effects of purity or investigate a grain boundary with a CA contribution. We were able to remove these restrictions by cutting bicrystals from recrystallized sheets of niobium. Measurements were made on ~ 15 such bicrystals. For symmetric bicrystals it was observed that the integral Q_{GB} was significantly higher than that of Das Gupta et al.'s bicrystals in qualitative agreement with the prediction of the ES interaction model (the CA interaction vanishes for a symmetric bicrystal). A method of investigating the CA interaction using asymmetric bicrystals was developed in which the $\delta H_{c2}/H_{c2}$ across the grain boundary could be changed by

changing the direction of the magnetic field in the plane of the grain boundary. The detailed results⁽⁴⁾ from one such bicrystal with 90% of the maximum possible CA interaction appeared to show that $(\hat{f}_p)_{CA} \approx (\hat{f}_p)_{ES}$ at $\alpha = 1$ in disagreement with the theory which predicted that $(\hat{f}_p)_{CA} \approx (\hat{f}_p)_{ES}$ only below $\alpha = 0.03$. It was subsequently discovered that this particular bicrystal was of non-uniform oxygen composition thus probably invalidating the measurement. Assymmetric bicrystals with uniform oxygen content were produced; the problem unfortunately was discovered too late for measurements to be made on them. Other problems, which made bicrystal measurements difficult, were the fact that the grain boundary curvature which must be present in any recrystallized sheet make the method of analysis somewhat uncertain (i.e., is the F_p peak height or the integral of the F_p peak the proper quantity for comparison between grain boundaries with different curvatures? Our procedure was to use the latter but it is hard to justify theoretically) and the very time consuming nature of the measurements (F_p must be measured at very closely spaced angular intervals).

To investigate the effects of purity and temperature we made measurements on polycrystalline thin foils and films with a columnar grain structure normal to the film surface. While these measurements were averages over many grain boundaries the anisotropy method could still be used and had the advantage of being rapid so that many specimens could be prepared and investigated. Both polycrystalline Pb-Bi alloy films^(8,11) and niobium foils doped with oxygen^(12,14) were studied.

Figure 1 shows the Q_{GB} in the niobium foils as a function of α , the impurity parameter. Clearly Q_{GB} is low for the high purity foils and increases markedly with doping by oxygen. It reaches a maximum value at $\alpha = 5$ and then drops precipitiously. Such behavior is not understandable if the CA interaction dominates grain boundary pinning ($(\hat{f}_p)_{CA}$ decreases with increasing α) but is qualitatively what is predicted by the ES interaction model. The fact that the peak in Q_{GB} occurs at $\alpha = 5$ rather than $\alpha = 10$ is easily understood if it is realized that H_c is being severely

suppressed by oxygen additions in this regime. Accounting for this H_c depression in the theory results in the curve shown in Figure 2. The experimental results and the theory are in as good agreement as can be expected considering the approximation in the theory.

The temperature dependence of Q_{GB} in the niobium foils (shown in Fig. 3) is consistent with the predictions of the ES model (Eq. 4) and inconsistent with those of the CA interaction model (Eq. 2). These two pieces of evidence make it appear certain that the ES interaction dominates flux pinning by grain boundaries over the entire range of commercial materials including the A = 15 compounds. The predicted magnitudes of $(\hat{f}_p)_{ES}$ from the ES model also account rather well for the magnitude of measurements of Q_{GB} in a wide variety of materials as shown in Figure 4. An additional bonus of the model is that it can also predict the magnitude of pinning by dislocation cell walls, thought to be the major pinning defect structure in commercial Nb-Ti alloys. These walls behave much like grain boundaries, with the densely packed dislocation cores in the walls scattering electrons leading to a reduced λ and increased κ near the wall.

Exploiting the fact that ES is the major mechanism of flux pinning we developed a new method of enhancing the flux pinning by columnar grain boundaries⁽⁹⁾ in thin films. A thin layer of an element is deposited on the base film. In our experiments the base film was Pb-Bi and the element was either pure Pb or pure Tl. When the bilayer film is aged in the correct temperature range (where grain boundary diffusion is very rapid and lattice diffusion is slow) the element will diffuse rapidly down the grain boundaries and spread out slowly laterally into the grains, thus forming a concentration profile around each boundary. This diffusion will either depress κ (Pb) or enhance it (Tl). Very little change in F_p is observed when atoms have diffused down the grain boundary producing a layer of monolayer segregation. This observation is in accord with the assumption of $\beta = 1$ for a high angle grain boundary

in the ES model. (If the dislocation cores already scatter electrons efficiently adding a monolayer of foreign atoms will not do much to change β .)

Maximum pinning enhancement in the Tl-coated films is only achieved when Tl has a chance to diffuse approximately a coherence length from the boundary. Enhancements of F_p by up to a factor of 4 are observed in this system. For the Pb coated films, Bi is the most mobile atom in the system and diffuses out of the bulk to the grain boundary and into the coating leaving a bismuth depleted region around each grain boundary. The flux pinning evolution in this case is complex. At low reduced fields the pinning rises to a maximum in times required for Bi to diffuse approximately one coherence length in the bulk; for reduced fields greater than 0.5, F_p first decreases rapidly and then slowly increases to a maximum higher than the original F_p before interdiffusion. All these results are qualitatively in accord with the predictions of the ES model which is modified in this case to allow the electron scattering due to the composition profile as well as the grain boundary itself to be taken into account⁽⁹⁾.

While the interdiffusion method offers a novel technique for enhancing grain boundary flux pinning in technologically important materials, it seems equally important to point out ways in which grain boundary pinning in the A-15 compounds can be improved by more simple methods. A-15 compounds as usually produced have resistivity ratios between 20 and 5. Due to the very small $\xi_0 \approx 50\text{\AA}$ of these compounds these resistivity ratios correspond to α 's between 0.045 and 0.18 well below the maximum in grain boundary pinning that should occur at $\alpha \approx 10$. Thus it would seem well worthwhile to attempt to produce "dirtier" A-15 compounds. Not only would this raise H_{c2} , thus raising F_p at high h , but it would also substantially improve grain boundary pinning at constant reduced field. On the other hand there would seem little point in attempting to modify the crystallographic texture of the A-15 deposit in hopes of enhancing Q_{CB} by the CA anisotropy mechanism, as has been

suggested elsewhere. Even at the relatively low α 's of the commercial A-15 materials the ES mechanism is the dominant one in grain boundary flux pinning. One further note of caution is necessary however. As predicted by Eq. 3 and shown experimentally by the niobium foils, increases in α produced by doping with elements that produce large decreases in H_c will decrease, not increase Q_{GB} . The H_c and T_c of the A-15 compounds are notoriously sensitive to degradation by such doping. Only if doping elements can be found that leave H_c and T_c almost unchanged will the doping strategy outlined above for improving Q_{GB} in the A-15 compounds be successful.

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2. E.J. Kramer, "Summation Curves for Flux Pinning in Superconductors", J. Appl. Phys., 49, 748 (1978).
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13. W.E. Yetter and E.J. Kramer, "Grain Boundary Flux Pinning: A Comparison of the Crystal Anisotropy and the Electron Scattering Mechanisms", in preparation.

14. D.A. Thomas and E.J. Kramer, "The Effect of Purity and Temperature on Grain Boundary Flux Pinning in Niobium Foils", in preparation.

Personnel supported under this grant:

Dr. Roland Schindler, postdoctoral associate, from Max Planck Institut fur Metallforschung, Stuttgart, West Germany. Now at National Semiconductor, Palo Alto, CA.

Dr. Michael Lunnon, postdoctoral associate, from H.H. Wills Laboratory of Physics, University of Bristol, Bristol, England. Now at Philips Research Labs, Mountain View, CA.

Dr. Wilson E. Yetter, B.S. Physics, SUNY, Binghamton, received his Ph.D. at Cornell University in 1980 for work supported by this grant. Postdoctoral associate from June to Dec. 1981. Now at GM Research Labs, Warren, MI.

Dr. Donald A. Thomas, B.S. Physics, Case Western Reserve University, received his Ph.D. at Cornell University in 1982 for work supported by this grant. Currently seeking employment.

Mr. Mark Glad, B.S. Physics, St. Olaf College. 2nd year graduate student in the Department of Materials Science and Engineering, Cornell University.

Interactions

The group working on grain boundary flux pinning at Cornell has interacted significantly with the following other groups:

Stanford - Dr. R. Hammond, Prof. Ted Geballe and Mr. John Talvecchio who are attempting to optimize flux pinning in thin A-15 films.

Westinghouse - Dr. Alex Braginski and his group working on producing thin film Nb_3Ge and other A-15's by chemical vapor deposition.

Wisconsin - Prof. David Larbalestier who is attempting to optimize the flux pinning by cell walls in NbTi materials.

Gottingen, West Germany - Effort in the Institut fur Metallphysik under Professors Peter Haasen and Herbert Freyhardt who are making in-situ A-15 composites and conducting flux pinning experiments on model systems (e.g., voids in niobium).

Cambridge University, England - Drs. Jan Evetts and Archie Campbell who are conducting measurements of noise and a.c. losses in samples where grain boundary flux pinning predominates.

MIT - Dr. Si Foner who is measuring $\delta H_{c2}/H_{c2}$ in single crystals of A-15 compounds, and is making in-situ A-15 composites.

Iowa State University - Ames Laboratory - Prof. John Clem, Doug Finnemore, and John Verhoener who are involved in theory and experiments on flux pinning, especially in in-situ composites.

Max-Planck Institut fur Metallforschung, Stuttgart, West Germany - Drs. Helmut Brandt and Ume Essmann who do theory and experiments on model systems, particularly on the summation problem.

Kernforschungszentrum, Karlsruhe, West Germany - Dr. Heinz Kupfer and Dr. Schaner who are attempting to optimize and understand flux pinning in the A-15 compounds.

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